

## CO-LIQUEFACTION OF COAL AND HIGH-DENSITY POLYETHYLENE

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### INTRODUCTION

High-density Polyethylene (HDPE) is a versatile polymer used as the material for containers, bottles, caps and films. Most HDPE is discarded after a single use and generally finds its way to a landfill. It has been estimated that waste plastics, including HDPE, comprise about 11% by weight but 21% by volume of landfills in the US. The properties that make HDPE a problem in the landfill are those that make HDPE a useful packaging agent, viz., its chemical stability and biological inertness. HDPE can be thermally degraded, of course, but a relatively high temperature is required. Further, the products of thermal degradation are not monomers but fragments of various molecular weights. Accordingly, using the HDPE as a co-liquefaction agent with coal could be promising.

Earlier work in this laboratory (1) has enumerated the properties/requirements of an ideal waste material as a co-liquefaction agent. It should be available in large supply; it should be manufactured cheaply, but should be expensive to dispose off, in a landfill or otherwise; and it should have one or more favorable properties -- a catalytic function, or hydrogen-transfer characteristics, or free-radical formation -- such that co-liquefaction is superior to the separate processes of coal liquefaction and the liquefaction of the waste material. HDPE certainly meets the first two of these criteria. In the present work, we examine its role in the third criterion.

Previous work in our laboratory has used a variety of waste materials as co-liquefaction agents: sawdust (1); agricultural waste (1); poly(vinyl chloride) (2); and automobile tires. This last material has been extensively studied, both from a reaction kinetic standpoint (3) and in terms of process design (4). The use of these co-liquefaction agents were studied both thermally and using a ferric-sulfide-based catalyst. This catalyst has been shown (5) to be remarkably effective for direct coal liquefaction. The superior performance of this catalyst is perhaps due to the intimate contact of pyritic and pyrrhotitic materials formed during the disproportionation of ferric sulfide at temperatures above 10°C. However, for space considerations, in this preprint we consider only the non-catalytic co-liquefaction of HDPE and coal. The effects of temperature, reaction time and the ratio of HDPE to coal on the conversion and product type are shown.

### EXPERIMENTAL

Details can be found elsewhere, *e.g.*, (3). In brief, all reactions were carried out in duplicate (at least) in a batch-tubing microreactor. This consists of a short section of heavy pipe of volume 27 ml with screw-on caps at each end (for insertion and removal of solid and liquid reactants and products), and a thin tube welded at the pipe middle and perpendicular to the axis (for addition of vapor-phase reactants and/or inerts, and for removal of vapor-phase products). Typically, 3 g of total feed (coal alone, HDPE alone, or coal plus HDPE) were placed in the reactor, the vapor phase was added, and the reactor was sealed off. Two such reactors were placed in a vertical-agitation unit, and a fluidized sandbath was used to heat the reactor contents rapidly to the final temperature. Most runs were performed between 350°C and 450°C, for reaction times between 15 min and 1 h, at a pressure of 2000 psig (at reaction temperature, *i.e.*, "hot") of hydrogen and/or helium. Ratios of HDPE to coal (*P/C*) ranged from 0 to 1; it was felt that larger values of *P/C* are unrealistic from the standpoint of commercial availability.

After the required time of reaction had elapsed, the sandbath was lowered and the reactors were cooled. The gas phase was captured and analyzed by gas chromatography. Other products were identified and quantified by solubility in tetrahydrofuran (THF) and hexane. Three fractions were measured:  $f_{TI}$ , the fraction of entering material insoluble in THF;  $f_{HI}$ , the fraction of material soluble in THF but insoluble in hexane; and  $f_G$ , the fraction of material present in the gas phase. A fourth parameter,  $f_{HS}$ , the fraction of material soluble in both THF and hexane, was obtained by difference:

$$f_{HS} = 1 - f_{TI} - f_{HI} - f_G \quad (1)$$

(For liquefaction runs involving coal only, the conversion,  $X$ , is typically given by:

$$X = 1 - f_{TI} \quad (2a)$$

the yield of the asphaltene fraction,  $A$ , by:

$$A = f_{HI} \quad (2b)$$

and the oil fraction yield,  $O$ , by:

$$O = f_{HS} \quad (2c)$$

However, as discussed below, we do not use this nomenclature here, and especially for runs involving HDPE, either alone or in combination with coal.) For co-liquefaction runs involving both coal and HDPE, overall fractions  $f_{HS}$ ,  $f_{TI}$ ,  $f_{HI}$ , and  $f_G$  were obtained as defined above. However, in order to compare co-liquefaction results using different ratios of HDPE to coal with one another and with liquefaction results using only coal, these fractions were also calculated on a coal-alone basis. The coal-alone fractions were obtained by subtracting off, in a proportional sense, the contribution of the HDPE as determined in the HDPE-only runs. If there are no additional effects when HDPE is added to coal, then co-liquefaction results on a coal-alone basis should be identical to (liquefaction) results for the coal-only experiments. Put differently, when HDPE is added to coal, any additional effects show up as differences, positive or negative, between the co-liquefaction results calculated on a coal-alone basis and the (liquefaction) results of the coal-only runs. This is consistent with the approach used in our previous work (1 - 4).

## RESULTS AND DISCUSSION

Particular attention was paid to base-case runs involving coal only and HDPE only. A statistically designed set of experiments using the Box-Behnken three-factor approach was used to obtain the dependence of both these materials on the three parameters of temperature, time, and hydrogen partial pressure, keeping the total pressure constant at 2000 psig by using helium. Ranges of the parameters were 350-450°C, 15-60 min., and 0-2000 psig, respectively. The results were fitted to a second-order polynomial in normalized temperature, normalized time, and normalized hydrogen partial pressure:

$$f = A_0 + A_T T^* + A_t t^* + A_P P^* + A_{TT} T^{*2} + A_{Tt} T^* t^* + A_{TP} T^* P^* + A_{tt} t^{*2} + A_{PP} P^{*2} \quad (3)$$

where the normalized time is given as:

$$t^* = \{t[\text{min}] - 30\} / 30 \quad (4)$$

and the other normalized parameters are similarly defined in terms of their center point values. The complete set of data and the statistical analyses can be found elsewhere (6). The values of the statistically significant parameters for coal and HDPE are shown in Table 1. The values for coal are consistent with those obtained by other workers in our laboratory (2,7,8).

From Table 1, it can be seen that the products of coal-only liquefaction are about equally divided between HI and HS, but most of the material is TI. Further the temperature is the most important parameter for HI, HS and G. Also from Table 1, the major product of HDPE-only liquefaction is HS, with more than half of the material being TI.

At room temperature, almost all the coal is found to be TI, *i.e.*, negligible amounts of coal are soluble in THF or hexane. However, when the experiment was repeated with HDPE, the value of  $f_{HI}$  was found to be approximately 0.97, while  $f_{HS}$  was found to be approximately 0.005, the remainder being  $f_{TI}$ . Since the amount of TI actually increases between room temperature and the temperatures of liquefaction, it is not reasonable to consider the conversion of HDPE to be given by the righthand side of Eqn (2a). Clearly, the temperature converts the THF-soluble, hexane-insoluble material to THF-insoluble material and (THF-soluble) hexane-soluble material.

Figure 1 shows the effect of the ratio of HDPE to coal,  $P/C$ , on the products formed. The results are on a coal-alone basis so, as noted earlier, an increase in an  $f$  value over the corresponding one for only coal ( $P/C = 0$ ) implies that co-liquefaction results in a net increase in that parameter, even when the effect of the HDPE is taken into account. From Figure 1,  $f_{TI}$  and  $f_G$  increase steadily with an increase in  $P/C$ . The increase in  $f_G$  is large relative to the value for only coal,

but about equivalent to that in  $f_{TI}$  on an absolute basis. The value of  $f_{HS}$  decreases with increasing  $P/C$ .

Figure 2 shows the effect of temperature on the co-liquefaction when  $P/C$  is kept at its highest value (= 1). At higher temperatures,  $f_{HS}$  increases dramatically, while  $f_G$ ,  $f_{HI}$ , and  $f_{TI}$  fall.

Finally, Figure 3 shows the effect of time at the highest temperature and largest  $P/C$  value. Larger reaction times increase HS and G, and decrease the amount of TI.

## CONCLUSIONS

At room temperature, HDPE consists of primarily THF-soluble, hexane-insoluble matter. When heated to around 400°C, the HI material forms HS material and some TI material.

For co-liquefaction of HDPE with coal, high  $P/C$  ratios, high temperatures, and large times of reaction appear to be helpful in terms of increasing the relative amount of HS material.

## ACKNOWLEDGMENTS

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Table 1. Coefficients of Eqn (3) for Liquefaction Using Coal and HDPE Separately

$f$	$A_O$	$A_T$	$A_I$	$A_P$	$A_{TI}$	$A_{TP}$	$A_{IP}$	$A_{TT}$	$A_{II}$	$A_{PP}$
For Coal										
HI	13.48	-3.37	-2.79	2.63	-1.47	--	0.83	-7.22	1.68	1.01
G	3.17	5.29	1.44	0.42	1.30	--	0.62	2.81	--	0.65
HS	13.19	6.07	4.84	1.52	--	--	--	-1.75	-3.79	--
For HDPE										
HI	1.87	0.16	0.49	--	-0.20	--	--	-0.61	-0.89	-0.55
G	3.35	1.85	1.04	0.71	--	--	--	0.70	--	0.50
HS	42.55	28.56	5.13	1.68	--	--	--	4.67	-4.86	--

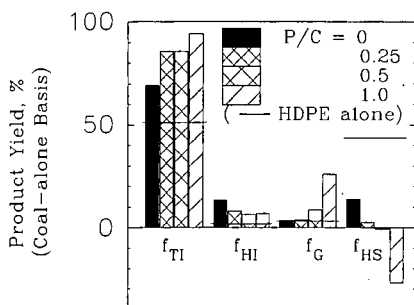


Figure 1. Effect of feed ratio,  $P/C$ , on product yields. Reaction conditions: 400°C, 1000 psig  $H_2$ , 30 min.

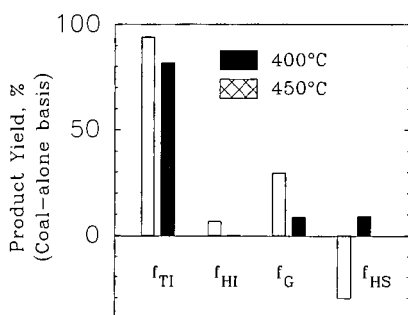


Figure 2. Effect of temperature on product yields. Reaction conditions: 1000 psig  $H_2$ , 30 min,  $P/C = 1$ .

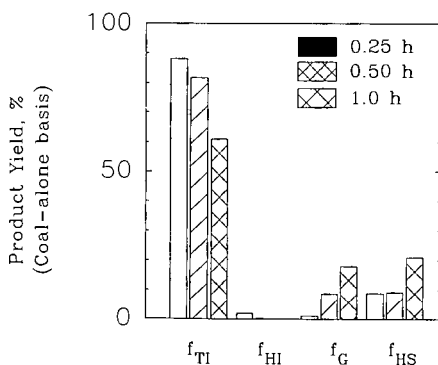


Figure 3. Effect of time on product yields. Reaction conditions: 450°C, 1000 psig  $H_2$ ,  $P/C = 1$ .